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(21) International Application Number: PCT/GB96/02899 (22) International Filing Date: 22 November 1996 (22.11.96) (30) Priority Data: 9524028.9 23 November 1995 (23.11.95) GB (71) Applicant (for all designated States except US): BRUNEL UNIVERSITY [GB/GB]; Uxbridge, Middlesex UB8 3PH (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): MILGROM, Lionel, Robert [GB/GB]; (GB). YAHIOGLU, Gokhan [GB/GB]; Brunel University, Uxbridge, Middlesex UB8 3PH (GB). (74) Agents: MALLALIEU, Catherine, Louise et al.; D. Young & Co., 21 New Fetter Lane, London EC4A 1DA (GB).		(81) Designated States: AU, CA, JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: SUBSTITUTED PORPHYRINS (57) Abstract A compound of general formula (I) wherein R ₁ , R ₂ , R ₃ and R ₄ are each independently H, optionally substituted alkyl, optionally substituted alkoxy, optionally substituted alkenyl, optionally substituted alkenyloxy, Si(alkyl) ₃ , halogen, CHO, COOR ₅ , OH, CN, NO ₂ , NO, NR ₅ R ₆ or formula (II) wherein (A) is optionally substituted aryl or optionally substituted heteroaryl; R ₅ and R ₆ are each independently hydrogen, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted aryl, halogen or hydroxy; X, Y, X ₁ , Y ₂ and Z are each independently H, optionally substituted alkyl, optionally substituted alkoxy, optionally substituted alkyl, optionally substituted alkoxy, optionally substituted alkenyl, optionally substituted alkenyloxy, Si(alkyl) ₃ , halogen, CHO, COOR ₅ , OH, CN, NO ₂ , NO, NR ₅ R ₆ , any adjacent two groups taken together form a-(OCH ₂ CH ₂) _n -group wherein n is 1, 2 or 3, or formula (III) wherein J is a single bond, =, CH ₂ O, OCH ₂ , COO, OOC, NHCO, CONH, CH ₂ or O; Q is H, optionally substituted alkyl, optionally substituted alkoxy, optionally substituted alkenyl, optionally substituted alkenyloxy, Si(alkyl) ₃ , halogen, CHO, COOR ₅ , OH, CN, NO ₂ , NO, NR ₅ R ₆ ; (B) is optionally substituted aryl or optionally substituted heteroaryl; provided that at least one of R ₁ , R ₂ , R ₃ or R ₄ is selected from formula (II); M is 2H with each of the two nitrogen atoms indicated being bonded to a single hydrogen, or M is a metal atom, metal compound or silicon or a compound of silicon and its uses, particularly in a liquid crystal device, as a reverse saturable absorber, a photodynamic therapy agent and in a biaxial nematic device.		

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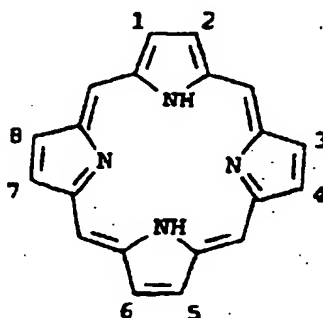
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SUBSTITUTED PORPHYRINS

This invention relates to novel substituted porphyrin compounds and their uses.

5 Porphyrin is given by the following general formula:



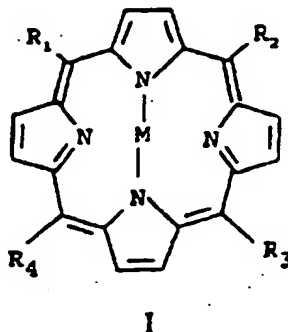
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Porphyrins have found uses in numerous applications including precursors for novel conducting polymers (Wagner et al, J. Am. Chem. Soc., 1994, 116, 9759; Anderson, Inorg. Chem., 1994, 33, 972 and Arnold et al, Tetrahedron, 1992, 48, 8781); non-linear optically active (NLO) materials (Anderson et al, Angew. Chem. Int. Ed. Engl., 20 1994, 33, 655 and Arnold et al, J. Am. Chem. Soc., 1993, 115, 12197); photosynthetic model compounds (Wagner et al, J. Org. Chem., 1995, 60, 5266, and Lin et al, Science, 1994, 264, 1105); and enzyme mimics (Anderson et al, Angew. Chem. Int. Ed. Engl., 1990, 29, 1400; Anderson et al, J. Chem. Soc., Chem. Commun., 1992, 946 25 and Mackay et al, J. Chem. Soc., Chem. Commun., 1992, 43).

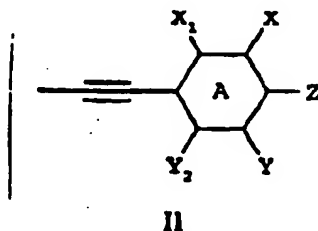
Meso-tetraalkynyl-substituted porphyrins are reported by Anderson in Tetrahedron Lett., 1992, 33 1101.

30 There exists a need for improved compounds which may be used in any of the above applications as well as other applications.

According to the present invention compounds of the following Formula I are provided:



wherein R_1 , R_2 , R_3 and R_4 are each independently H, optionally substituted alkyl, optionally substituted alkoxy, optionally substituted alkenyl, optionally substituted alkenyloxy, $\text{Si}(\text{alkyl})_3$, halogen, CHO, OH, CN, NO_2 , NO, NR_5R_6 or the following Formula II:



wherein



is optionally substituted aryl or optionally substituted heteroaryl;

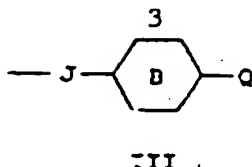
R_5 and R_6 are each independently hydrogen, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted aryl, halogen or hydroxy;

X, Y, X_1 , Y_2 and Z are each independently H, optionally substituted alkyl, optionally substituted alkoxy, optionally substituted alkenyl, optionally substituted alkenyloxy,

$\text{Si}(\text{alkyl})_3$, halogen, CHO, OH, CN, NO_2 , NO, NR_5R_6 , any adjacent two groups taken

together form a $-(\text{OCH}_2\text{CH}_2)_n-$ group wherein n is 1, 2 or 3, or the following Formula

III:



5 wherein J is a single bond, \equiv , CH_2O , OCH_2 , COO , OOC , NHCO , CONH , CH_2 or O;

Q is H, optionally substituted alkyl, optionally substituted alkoxy, optionally substituted alkenyl, optionally substituted alkenyloxy, $\text{Si}(\text{alkyl})_3$, halogen, CHO , OH , CN , NO_2 , NO , NR_5R_6 ;

10



is optionally substituted aryl or optionally substituted heteroaryl;

provided that at least one of R_1 , R_2 , R_3 or R_4 is selected from Formula II;

15 M is 2H with each of the two nitrogen atoms indicated being bonded to a single hydrogen, or M is a metal atom, metal compound or silicon or a compound of silicon.

The metal atom may be present for example as the metal with an oxidation state of +2 or it may be present with other ligands (or anions) attached to it. These ligands

20 (anions) may serve the purpose of altering the hydrophobicity of the molecule as a whole. Examples of suitable anions include bromine, chlorine or oxide. Examples of suitable metals include Ni, Pb, V, Pd, Co, Nb, Al, Sn, Zn, Cu, Mg, Ca, In, Ga, Fe, Eu, Lu, Pt, Ru, Mn and Ge.

25 Compounds of general Formula I may also be protonated so that they carry a +1 or +2 charge.

When any one or more of R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , Z, X_1 , Y_2 , X, Y or Q is alkyl, or contains an alkyl moiety, it can be straight or branched chain and is preferably C_{1-20}

30 alkyl. R_1 , R_2 , R_3 , R_4 , R_5 and R_6 are more preferably C_{1-6} alkyl, even more preferably C_{1-4} alkyl, for example methyl, ethyl, propyl, iso-propyl, n-butyl, isobutyl, sec-butyl

or t-butyl. Z, X₁, Y₂, X, Y or Q are more preferably C₇₋₂₀ alkyl for example, -C₇H₁₅-, -C₈H₁₇-, -C₉H₁₉-, -C₁₀H₂₁-, -C₁₁H₂₃-, -C₁₂H₂₅-, -C₁₃H₂₇-.

- 5 When any one of R₁, R₂, R₃, R₄, R₅, R₆, Z, X₁, Y₂, X, Y or Q is a substituted alkyl group, or contains a substituted alkyl moiety, it may comprise one or more substituents chosen from halogen, NO₂, CN, -COOR₅ or a salt thereof, hydroxy or alkoxy.

- 10 When any one of R₁, R₂, R₃, R₄, Z, X₁, Y₂, X, Y or Q is a substituted alkenyl group, or contains an alkenyl moiety, it may be straight or branched chain and is preferably C₂₋₂₀ alkenyl. R₁ to R₆ are more preferably C₂₋₆, even more preferably C₂₋₄ alkenyl, for example vinyl, but-3-enyl or 3-methyl-but-3-enyl. Z, X₁, Y₂, X, Y or Q are more preferably C₇₋₂₀ alkenyl.

- 15 When any one of R₁, R₂, R₃, R₄, Z, X₁, Y₂, X, Y or Q is a substituted alkenyl group, or contains a substituted alkenyl moiety, it may comprise one or more substituents chosen from halogen, -COOR₅ or a salt thereof, hydroxy, NO₂ and CN.

- 20 When any one of R₁, R₂, R₃, R₄, Z, X₁, Y₂, X, Y or Q is an optionally substituted alkoxy or alkenyloxy group, or contains a substituted alkoxy or alkenyloxy moiety, it may be straight or branched chain and is preferably C₁₋₂₀ alkoxy or alkenyloxy. R₁ to R₆ are more preferably C₁₋₆ alkoxy or alkenyloxy. Z, X, Y, X₁, Y₂ or Q are more preferably C₇₋₂₀ alkoxy alkenyloxy.

- 25 When any one of R₁, R₂, R₃, R₄, Z, X₁, Y₂, X, Y or Q is the group COOR₅, it is preferably COOH; an alkoxycarbonyl group, for example methoxycarbonyl and ethoxycarbonyl; or a haloalkenyloxycarbonyl group, for example 3,4,4-trifluorobut-3-enyloxycarbonyl, 3-methyl-4,4-difluorobut-3-enyloxycarbonyl.

- 30 When A or B is aryl, or contains an aryl moiety, it is preferably C₆₋₁₀ aryl, more preferably it is phenyl.

When A or B is heteroaryl, or contains a heteroaryl moiety, it is preferably a 5 or 6 membered ring containing at least O, N or S atom as the heteroatom, for example pyridine, pyrrole, pyrazine, imidazole, furan or thiophene.

- 5 When A or B is substituted aryl or heteroaryl it may comprise one or more substituents chosen from alkyl, alkoxy, haloalkyl, halogen, COOR₃ or a salt thereof, CN or NO₂. Examples of these groups are 4-methylphenyl, 4-chlorophenyl, 4-fluorophenyl, 4-nitrophenyl, 3-trifluoromethylphenyl, 4-trifluoromethylphenyl, 4-chlorobenzyl, 4-fluorobenzyl, 3-trifluoromethylbenzyl, 4-trifluoromethylbenzyl, 4-nitrobenzyl and 4-methylbenzyl.

When any one of R₁, R₂, R₃, R₄, R₅, R₆, Z, X₁, Y₂, X, Y or Q is halogen, or contains a halogen moiety, it is preferably fluorine, chlorine, bromine or iodine. Even more preferably, it is fluorine, chlorine or bromine.

15

- Thus when any one of R₁, R₂, R₃, R₄, R₅, R₆, Z, X₁, Y₂, X, Y or Q is a haloalkyl or haloalkenyl group it may contain one or more halogen atoms, preferably chlorine, fluorine or bromine. Examples of these groups are fluoromethyl, difluoromethyl, trifluoromethyl, chloromethyl, dichloromethyl, trichloromethyl, 2-fluoroethyl, 2,2,2-trifluoroethyl, pentafluoroethyl, 2,2-difluoroethyl, 3,3-dichloroprop-2-enyl, 2-chloroprop-2-enyl, 3,4,4-trifluorobut-3-enyl, 4-fluorobut-3-enyl, 4,4-difluorobut-3-enyl and 3-methyl-4,4-difluorobut-3-enyl.

- 25 Similarly when any one of R₁, R₂, R₃, R₄, R₅, R₆, Z, X₁, Y₂, X, Y or Q is a haloalkoxy group it may contain one or more halogen atoms, preferably chlorine, fluorine or bromine.

- When any one of R₁, R₂, R₃, R₄, R₅, R₆, Z, X₁, Y₂, X, Y or Q is -NR₃R₆ it is preferably NH₂; a mono-alkylamino group, for example methylamino or ethylamino; 30 or a di-alkylamino group, for example dimethylamino or diethylamino.

When any one of R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , Z , X_1 , Y_2 , X , Y or Q is $\text{Si}(\text{alkyl})_3$ it is preferably $\text{Si}(\text{C}_{1-6} \text{ alkyl})$, for example trimethylsilyl, triethylsilyl or triisopropylsilyl.

Preferably R_1 , R_2 , R_3 , and R_4 are all a group of Formula II.

5

Preferably R_1 and R_3 are a group of Formula II and R_2 and R_4 are H or $\text{Si}(\text{CH}_3)_3$, or R_2 and R_4 are a group of Formula II and R_1 and R_3 are H or $\text{Si}(\text{CH}_3)_3$.

Preferably M is 2H or Zn.

10

Preferably when M is a silicon compound it is Si-alkoxy or Si-OH.

Preferably any one of X , Z or Y is C_{1-20} alkyl or alkoxy.

15 Preferably X and Z or Y and Z together form a - $(\text{OCH}_2\text{CH}_2)_n$ - group.

Porphyrins usually have a characteristic red colour due to an intense absorption (called the B band: a π - π^* transition) in the region 400-420nm. In the visible part of the spectrum, there are weaker absorptions (called Q bands) in the region 500-650nm, the number depending on whether the macrocycle is in the form of a free-base ($M = 2\text{H}$, 4 bands), a dication ($M = 4\text{H}$, 2 bands) or a metal complex ($M = \text{M}$, 2 bands). As described below in greater detail, one advantage of the effect of *meso*-arylethynyl groups is to extensively red-shift the whole UV/visible spectrum by as much as 50 nm. The intensity of the Q bands is also increased relative to the B band.

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25 This turns the characteristic porphyrin red colour to a brilliant green: hence the trivial name, chlorophyrin - green porphyrin.

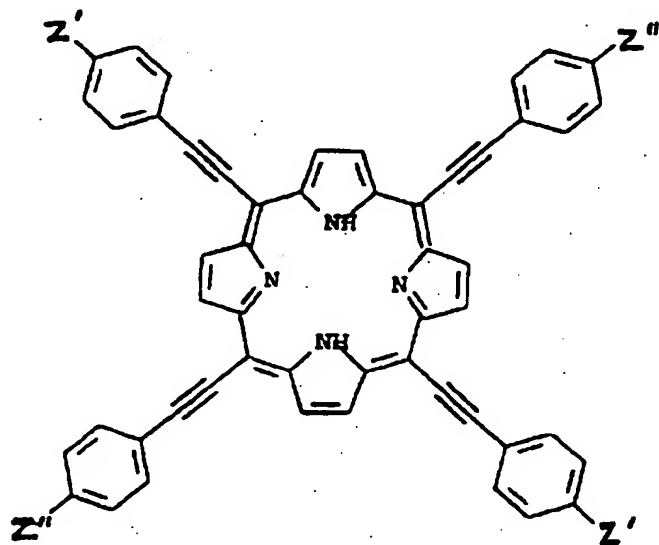
The compounds of the present invention may be used in a broad range of applications including those applications mentioned in the introduction of this application. Other uses include pigments or dyes, as components of discotic liquid crystal phases (in particular they may also be used as precursors for discotic liquid crystals), two dimensional conjugated polymeric arrays, see Drain and Lehn, J. Chem. Soc., Chem.

30

Commun., 1994, 2313; as reverse saturable absorbers and as agents for photodynamic therapy. The types of liquid crystal devices include linear and non-linear electrical, optical and electro-optical devices, magneto-optical devices and devices providing responses to stimuli such as temperature changes and total or partial pressure changes.

The compounds of the present invention may also be used in biaxial nematic devices and as second or third order non-linear optic (NLO) materials.

The materials illustrated below when Z' is an electron donating group such as alkyl, alkoxy, for example C₁₋₁₅, dialkylamine or diarylamine and Z'' is an electron withdrawing group such as NO₂, CN, halogen, NO, NH₂, an ester or carboxylic acid may be useful as biaxial nematic liquid crystal materials possessing NLO properties. Particularly when Z'' is an electron withdrawing group and Z' is an electron donating group, then the materials below may be of use as second and/or third order NLO materials.



Examination of the UV/visible data in Table 1 shows that 4-alkoxyaryl groups red-shift the spectra of chlorophyrins far more than in the equivalent *mesotetraarylporphyrins*. Clearly, the acetylenic groups vastly improve "communication" between aryl substituents and the macrocycle. This electronic coupling of macrocycle, acetylenic groups and aryl substituents may provide, at least in symmetric molecules, materials with large 2nd order hyperpolarisabilities.

Compounds of the present invention may also be liquid crystalline materials with NLO properties.

Materials have been proposed for laser addressed applications in which laser beams are used to scan across the surface of the material or leave a written impression thereon. For various reasons many of these materials have consisted of organic materials which are at least partially transparent in the visible region. The technique relies upon localised absorption of laser energy which causes localised heating and in turn alters the optical properties of the otherwise transparent material in the region of contact with the laser beam. Thus as the beam traverses the material, a written impression of its path is left behind. One of the most important of these applications is in laser addressed optical storage devices, and in laser addressed projection displays in which light is directed through a cell containing the material and is projected onto a screen. Such devices have been described by Khan, Appl. Phys. Lett., 1973, 22, 111; and by Harold and Steele in Proceedings of Euro display, 84, 29-31, September 1984, Paris, France, in which the material in the device was a smectic liquid crystal material. Devices which use a liquid crystal material as the optical storage medium are an important class of such devices. The use of semiconductor lasers, especially $\text{Ga}_x\text{Al}_{1-x}\text{As}$ lasers where x is from 0 to 1, and is preferably 1, has proven popular in the above applications because they can provide laser energy at a range of wavelengths in the near infra-red which cannot be seen and thus cannot interfere with the visual display, and yet can provide a useful source of well-defined, intense heat energy. Gallium arsenide lasers provide laser light at wavelengths of about 850nm, and are useful for the above applications. With increasing Al content ($x < 1$), the laser wavelength may be reduced down to about 750nm. The storage density can be increased by using a laser of shorter wavelength.

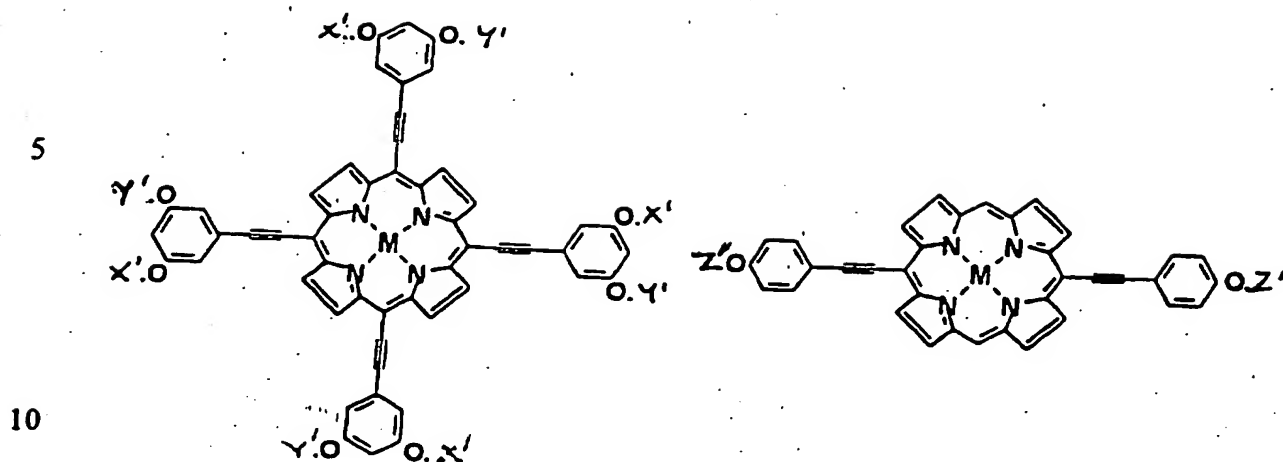
The compounds of the present invention may be suitable as optical storage media and may be combined with dyes for use in laser addressed systems, for example in optical recording media. Typically the porphyrin will absorb in the near-infrared. In order to make an optical recording media using a near-infrared absorber, the near-infrared absorber may be coated or vacuum-deposited onto a transparent substrate. EP 0 337

209 A2 describes the processes by which the above optical-recording media may be made. Further, the compounds of the present invention are useful in near-infrared absorption filters and liquid crystal display devices. As described similarly in EP 0 337 209 A2, display materials can be made by mixing a near-infrared absorber of
5 Formula I with liquid crystal materials such as nematic liquid crystals, smectic liquid crystals and cholesteric liquid crystals. The compounds of the present invention may be incorporated into liquid crystal panels wherein the near infrared-absorber is incorporated with the liquid crystal and a laser beam is used to write an image. Mixtures of porphyrins of the current invention may be mixed with liquid crystal
10 materials in order to be used in guest-host systems. GB 2,229,190 B describes the use of phthalocyanines incorporated into liquid crystal materials and their subsequent use in electro-optical devices.

Previously *meso*-substituted porphyrins have not been seriously exploited as potential
15 mesogens.

The phenyl ring is an excellent platform for appending mesogenic groups (e.g., X, Y or Z = alkyl or alkoxy) but in *mesotetraaryl*porphyrins, it is approximately orthogonal to the plane of the porphyrin macrocycle. It is believed that separating the
20 phenyl ring from the macrocycle, via an acetylenic link, would allow it to become coplanar with the macrocycle to provide a discotic mesogen. Preferably long alkoxy chains are placed in the aryl 3- and 5-positions to provide a discotic mesogen.

Preliminary investigations of compounds where a group of Formula II (where Z = OC₁₀H₂₁ and X, Y, X₁, Y₂ = H) are in the four *meso* positions reveal that it has a
25 classic columnar discotic phase (probably D_h symmetry) with a discotic range from 110-230°C. The following two compounds where X', Y' and Z' are alkyl also show a columnar discotic phase.

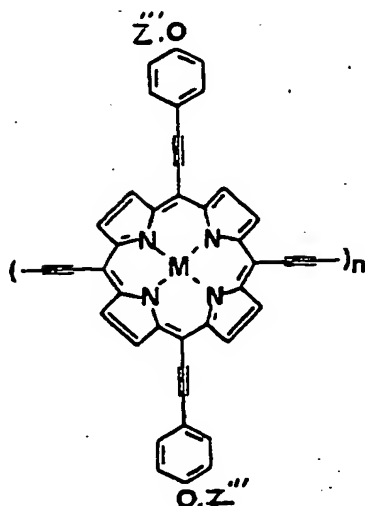


- 15 Another preferred compound is 10,20-*mesobis*(arylethynyl)porphyrin as a calamitic mesogen.

Langmuir Blodgett films incorporating porphyrins of the present invention may be laid down using conventional and well known techniques, see R.H. Tredgold in
20 "Order in Thin Organic Films", Cambridge University Press, p74, 1994 and reference therein.

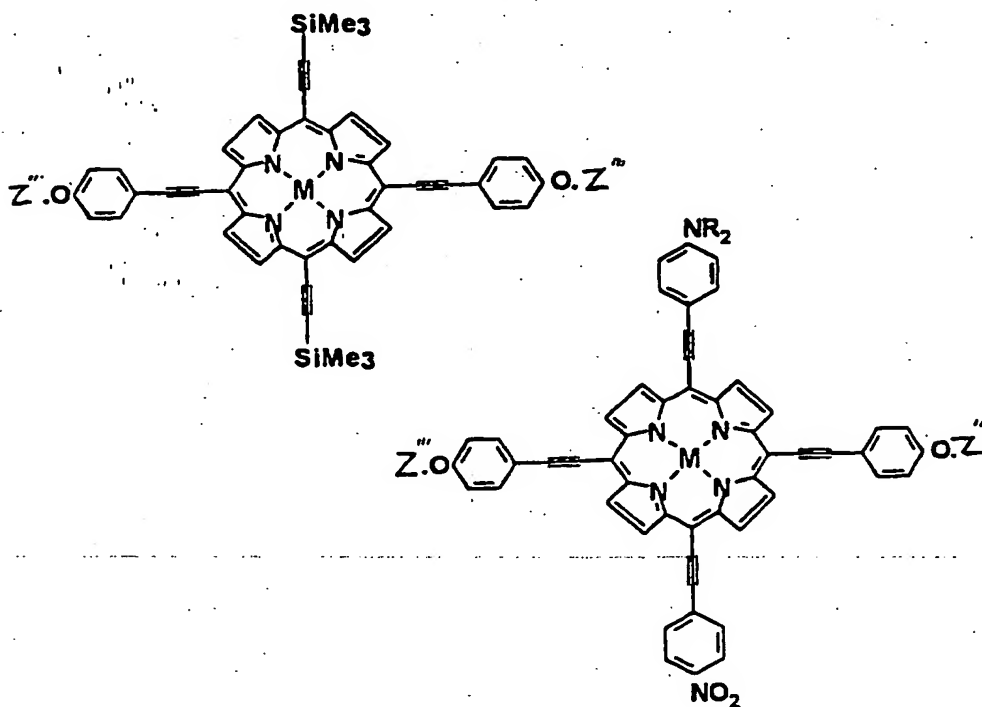
It may be advantageous to polymerise certain of the compounds described by the current invention. Polymerised porphyrins may also be used in, for example,
25 Langmuir Blodgett films. There are numerous ways in which the porphyrin may be incorporated into a polymer. Polymerisation may be effected by one or more of the positions R₁-R₄ in Formula I for example via one or more of the OH groups or via the central metal atom or metal compound or polymerisation may be achieved by a combination of the above techniques. An example of a suitable substituent which may
30 be used to effect polymerisation is an unsaturated substituent such as an alkene group.

An example of a repeating unit of one such polymer is shown below:



Main chain or side chain liquid crystal polymers may also be made using the compounds of the present invention or metal-metal linked liquid crystal polymers.

- 15 We have synthesised unsymmetrical chlorophyrins, i.e., with one type of aryethynyl moiety in the 5- and 15-*meso*-positions and a different aryethynyl moiety in the 10- and 20-positions. Examples are shown below (where $Z''' = \text{alkyl}$):



By judicious use of 5,15-ethynyl substituents with protecting groups (e.g. $\text{Me}_3\text{Si}-$), we can produce porphyrins with two bare acetylenes. These can be polymerised or copolymerised (e.g.. with poly(phenylene vinylene)) to make electroluminescent polymers. Alternatively, the bare acetylenic substituents may be reacted individually
5 with electron donor and acceptor groups to furnish "push-pull" acetylenic porphyrins with large 1st-order hyperpolarisabilities.

Langmuir Blodgett Films incorporating compounds of the present invention may be used as optical or thermally addressable storage media.

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The compounds of the present invention may also be used as molecular wires, see R.J.M. Nolte et al. *Angew. Chem. Int. Ed. Eng.*, 1994, 33(21), 2173.

Water soluble paramagnetic manganese complexes of the porphyrins of the present
15 invention, including Mn(III) porphyrins, may be used in methods for enhancing images obtained from magnetic resonance imaging of a region of regions containing a malignant tumour growth.

The compounds of the present invention may be used as photodynamic therapeutic
20 (PDT) agents. The combination of a sensitizer and electromagnetic radiation for the treatment of cancer is commonly known as photodynamic therapy. In the photodynamic therapy of cancer, dye compounds are administered to a tumour-bearing subject, these dye substances may be taken up, to a certain extent by the tumour. Upon selective irradiation with an appropriate light source (e.g. a laser) the
25 tumour tissue is destroyed via the dye mediated photo-generation of a species such as singlet oxygen or other cytotoxic species such as free radicals, for example hydroxy or superoxide. This requires the sensitizer to have a high triplet yield and lifetime in order to have the best chance of sensitising singlet oxygen production. It also requires a source of laser illumination into the tumour, the cheapest and most penetrating laser
30 light being red.

Porphyrins absorb strongly in the blue, which means they are not well "tuned" to work with red light and so their PDT effect is not very penetrating. Thus macrocycles with intense, longer-wave absorptions (e.g., chlorins, phthalocyanines, benzoporphyrins, etc.), are increasingly being tested as PDT sensitizers. Chlorophyrins have better red-light absorbing properties than porphyrins, and would be well-suited for PDT. Further, chlorophyrins showing excellent triplet-state yields and lifetimes.

Examples of fluorescent lifetimes are given below in Table 1.

10		<u>Table 1</u> <u>Compound 2a</u> <u>where M = Zn</u>	<u>Compound II of</u> <u>Table I</u>
15	Fluorescence quantum yield, Φ_f	0.0988	0.079
	Fluorescence lifetime, τ_f	1.8 ns \pm 30% (calc)	1.6 ns \pm 30 (calc).
20	Phosphorescence quantum yield Φ_T	0.88 \pm 10%	0.78 \pm 10%
	Phosphorescence Lifetime τ_T	680 \pm 15% μ sec	700 \pm 11% μ sec
25	ϵ_{max} (extinction coefficient ground state)	290,000 \pm 3%	490,000 \pm 4%
	ϵ_T (extinction coefficient excited state)	127,000 \pm 8% (at 530 nm)	156,000 \pm 8% (at 540 nm)
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PCT/GB94/01847 describes substituted metallophthalocyanines and phthalocyanines as PDT agents. Many of the techniques described therein (and references cited) are applicable to the current materials.

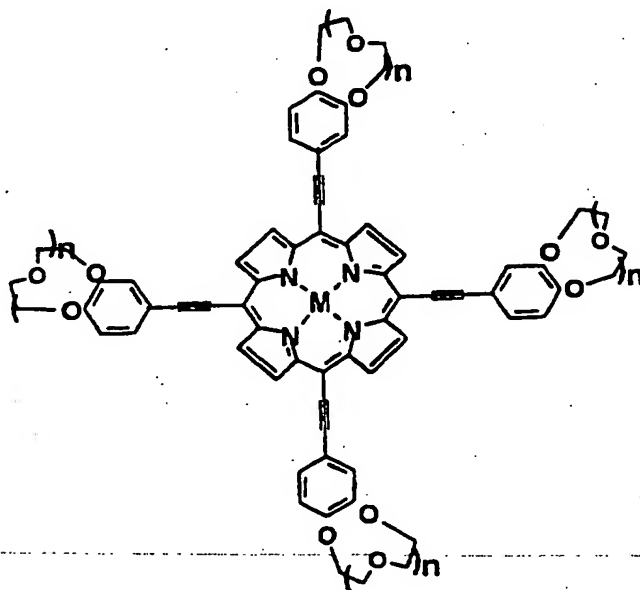
Metalloporphyrins, particularly the Pt and Pd complexes, have been used in phosphoimmunoassays (PIA) [AP Savitsby et al, Dokl. Acad. Nauk SSSR, 1989, 304, 1005]. Also the extreme sensitivity of these metalloporphyrins' triplet excited states to dissolved oxygen has been used to measure dissolved O₂ levels in biological systems

[TJ Green et al, Anal. Biochem., 1988, 174, 73; EP 0 127 797A and US-A-4,707,454]. Because porphyrins substituted with four *meso*arylethynyl groups have very high triplet yields, we envisage they will have improved characteristics of PLA and/or sensitivity to dissolved O₂.

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In one preferred embodiment the compound of Formula contains at least one crown-ether. A preferred example is shown below:

It is believed that chlorophyrins with aryl crown-ether substituents will complex suitable metal cations. This will be efficiently 'communicated' to the macrocycle, via the acetylenic groups. Such a substituted chlorophyrin will experience significant alteration of the absorption and/or emission properties. Alternatively, NLO-active unsymmetrical chlorophyrins with two crown-ether substituents may change their NLO properties on metal complexation. Thus, crown-ether-substituted chlorophyrins could act as sensors for low concentrations of metals.

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Various further preferred features and embodiments of the present invention will now be described by way of non-limiting example with reference to the following

Examples and drawings, in which:

- 5 Figures 1, 2, 3, 4 and 5 show synthetic schemes for compounds in accordance with embodiments of the present invention: and

Figure 6 illustrates a liquid crystal device in which the materials of the current invention may be incorporated.

10

Reagents and conditions used in the synthetic routes of Figures 1 and 2 are as follows:

- i) BuLi/THF/-78°C
- ii) DMF/room temperature
- iii) H⁺/H₂O
- 15 iv) C₉H₁₉Br/K₂CO₃/DMF/70-80°C
- v) Zn/(C₆H₅)₃P/CBr₄/DCM

Reagents and conditions used in the synthetic route of Figure 4 are as follows:

- i) Pyrrole (large excess), BF₃.OEt₂, -25°C, 15 minutes - 1 hour
- 20 ii) BF₃.OEt₂, CH₂Cl₂, -25°C

Butyllithium was ordered as a 1.6 molar solution in THF from Aldrich Chemical Co., The Old Brickyard, New Road, Gillingham Dorset, U.K..

DMF = dimethylformamide,

25 THF = tetrahydrofuran,

K₂CO₃ = anhydrous potassium carbonate,

4-octylphenylacetylene was obtained from Maybridge Chemical Company Ltd,

Trevillet, Tintagel, Cornwall, U.K.

All other chemicals were obtained from Aldrich.

30

Preparations

16

4-Octylphenylpropynal 3: see Figure 1 for synthesis from 4-octylphenylacetylene.

Yield = 0.85g (84%). IR (neat thin film); 2200 ($\text{-C}\equiv\text{C-}$ stretch), 1600 (unsaturated -C=O stretch) cm^{-1} : Mass spec. m/e required $M^+ = 242$; found $M^+ = 242$; $[\text{M-CO}]^+ = 214$; $[\text{M-C}_4\text{H}_9]^+ = 185$; $[\text{M-CO-C}_4\text{H}_9]^+ = 157$. $^1\text{Hnmr}$, $_{\text{H}}(\text{CDCl}_3)$: 9.41 (s, 1H, -CHO), 7.37 (q, 4H, centre of aryl AB spin system, $J_{\text{AB}} = 7.9\text{Hz}$), 2.64 (t, 2H, $\text{-CH}_2\text{-}$ next to aryl ring), 1.61 (m, 2H, $\text{-CH}_2\text{-}$ flanked by two others in octyl chain), 1.26 (m, 12H, rest of octyl chain), 0.88 (t, -CH_3 , terminal methyl in octyl chain) ppm.

- 10 4-Octylphenylpropynal 3 was prepared from 4-octylphenylacetylene by quenching the acetylide (formed by low temperature reaction with BuLi, see Brandsma in "Preparative Acetylene Chemistry" 2nd Edition, Studies in Organic Chemistry 34, Elsevier Science Publishers (Amsterdam), 1998, Chapter 2, p13) with DMF, followed by acid hydrolysis. Lindsey porphyrin synthesis (Lindsey and Lee in tetrahedron, 15 1994, 50, 11427) with pyrrole gave porphyrin 2b in 8% yield and a small amount of a second porphyrin-like product that eluted more slowly from a silica column with dichloromethane (DCM).

4-Nonyloxyphenylpropynal 5: see Figure 2 for synthesis from 4-

- 20 hydroxybenzaldehyde. Yield = 1.54g (91%, from preceding 4). IR (neat thin film); 2190 ($\text{-C}\equiv\text{C-}$ stretch), 1660 (unsaturated -C=O stretch) cm^{-1} : Mass spec. m/e required $M^+ = 272$; found $M^+ = 272$; $[\text{M-C}_9\text{H}_{18}]^+ = 146$; $[\text{M-C}_9\text{H}_{18}\text{-CO}]^+ = 118$; $^1\text{Hnmr}$, $_{\text{H}}(\text{CDCl}_3)$: 9.39; (s, 1H, -CHO), 7.22 (q, 4H, centre of aryl AB spin system, $J_{\text{AB}} = 8.5\text{Hz}$), 3.99 (t, 2H, $\text{-CH}_2\text{-}$ next to oxygen on aryl ring), 1.79 (p, 2H, $\text{-CH}_2\text{-}$ flanked by 25 two others in nonyl chain near oxygen), 1.46 (p, 10H, rest of nonyl chain), (t, -CH_3 , terminal methyl in nonyl chain) ppm.

- 4-Nonyloxyphenylpropanal 5 was prepared in a three-step synthesis from 4- hydroxybenzaldehyde. Alkylation of the phenolic -OH with 1-bromononane was 30 followed by a Corey and Fuchs reaction with CBr_4 , triphenylphosphine and zinc (see Tetrahedron Lett., 1972, 3769) to give β,β -dibromostyryl derivative 4. Low temperature reaction of 4 with 2.5 equivalents of BuLi followed by quenching of the

acetylide with DMF and acid hydrolysis yielded 5. Care was taken not to allow the acidity of this reaction to drop below pH 6-7 otherwise no arylpropynal was produced (see Brandsma *ibid.* Chapter 4, p102). Lindsey porphyrin synthesis with pyrrole and 4, using $\text{BF}_3 \cdot \text{OEt}_2$ as catalyst, afforded porphyrin 2c in 3% yield. A second porphyrin-like product was separated as the major product via column chromatography on silica gel, eluting with DCM.

Examples

The synthesis of compounds in Figure 4 was carried out based on methods described earlier in this application and of Lindsey, apart from the reactions were carried out at -25°C as opposed to room temperature (as in Lindsey). All of the *meso*-substituted dipyrromethanes were isolated in the pure form by chromatography [silica gel: cyclohexane/ethyl acetate/triethylamine 80:20:1].

All of the porphyrins were isolated as green solids after column chromatography. Metallations were carried out according to standard procedures, for example see J.W. Buchler in "The Porphyrins" Ed. D. Dolphin, Academic Press, New York, 1978, 1, p390.

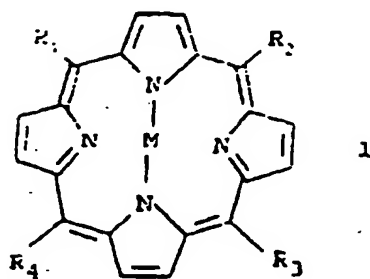
5,10,15,20-Mesotetra(4-octylphenylethynyl)porphyrin 2b: boron trifluoride dietherate (40µl, 0.33mM) was added to a stirred, nitrogen degassed solution of 4-octylphenylpropynal (0.61g, 2.5mM) pyrrole (0.17g, 2.5mM) in dry, distilled DCM (250ml) at -25°C. The reaction mixture was kept at this temperature during 4 hours, then allowed to warm to room temperature overnight. 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (570mg, 2.5mM) was then added, resulting in the reaction solution turning green. The solvent was removed under vacuum, and the residue purified by column chromatography (silica gel; DCM) to give a dark green sticky solid. Trituration with methanol and filtration gave the desired porphyrin as a dark green powder 58mg (8%), melting point = 171-172°C (with decomposition): IR (nujol mull); 2196cm⁻¹, weak: ^1H (CDCl₃); 9.27 (s, 8H, β-pyrrole-H), 7.67 (q, 16H, centre of aryl AB spin-system, J_{AB} = 7.9Hz), 2.78 (t, 8H, -CH₂- next to aryl ring), 1.78 (p, 8H, -CH₂- flanked by two methylene groups), 1.55-0.88 (m, 52H, rest of octyl

chain). FABMS, $[M^+]$ found 1158.7512; $C_{84}H_{94}N_4$ requires $[M^+] = 1158.7512$. A second minor porphyrin-like fraction was isolated from the column as a green powder. Yield = 5.2mg.

- 5 5,10,15,10-Mesotetra(4-nonyloxyphenylethynyl)porphyrin 2c: the synthetic procedure for this porphyrin was the same as for 2b using identical molar quantities of boron trifluoride dietherate (40 μ l, 0.33mM), 4-nonyloxyphenylpropynal (0.68g, 2.5mM), pyrrole (0.17g, 2.5mM), DDQ (570mg, 2.5mM) and DCM (250ml). Trituration of the
- 10 dark green oil initially obtained after column chromatography on silica with methanol yielded 2c as a green powder. Yield = 19(3%), melting point = 147-148°C; IR (nujol mull); 2192cm⁻¹: $^1H(CDCl_3)$; 9.11 (s, 8H, β -pyrrole-H), 7.48 (q, 16H, centre of aryl AB spin-system, $J_{AB} = 8.2$ Hz), 4.08 (t, 8H, -CH₂- next to aryl ring), 1.91 (p, 8H, -CH₂- flanked by two methylene groups), 1.55-0.84 (m, 60H, rest of nonyl chain), -3.00 (s, 2H, N-H). FABMS, $[M^+]$ found 1278.7512; $C_{88}H_{102}N_4$ requires $[M^+] = 1278.7512$. A
- 15 second minor porphyrin-like fraction was isolated from the column as a green powder. Yield = 33mg.

- Alkynyl *meso* substituents significantly red-shift the porphyrin B and Q bands (see Anderson, Tetrahedron Lett., 1992, 33, 1101). Thus, compared to
- 20 mesotetraphenylporphyrin (TPP), the B band of porphyrin 1 (shown below) is red-shifted by about 34nm. Replacing the trimethylsilyl group of 1 with an aryl group increases the B and Q band red shifts even further (46 {2a}, 54 {2b}, and 57 {2c} nm for the B band). In addition, there is a marked increase in the main Q band absorption relative to that of the B band, and two of the Q bands appear as smaller shoulders
- 25 either side of the main Q band absorption. This illustrates that the ethynyl groups mediate communication between the porphyrin and aryl pi-systems more effectively than when the aryl group is connected directly to the porphyrin macromolecule. We have also found that substituents on the aryl group can affect the red-shift. For
- 30 example in terms of red-shift alkoxy > alkyl > H. We have also found that a bigger increase in red-shifts occurs in trans-disubstituted substituted compounds compared to tetrasubstituted substituted compounds.

Details of compound 1 may be found in Anderson *ibid*.



where R_1 - R_4 are all $\equiv\text{SiMe}_3$

10

Solid samples and DCM solutions of the neutral porphyrins 2b and 2c are green. Acidification with several drops of trifluoroacetic acid turns solutions of 2b mustard yellow and solution of 2c pink.

- 15 The second porphyrin-like compounds obtained as by-products would appear from a combination of FAB mass spectroscopy (same m/e values as 2b and 2c) and $^1\text{Hnmr}$ (which shows separate doublets for each of the β -protons - a pattern not consistent with one or two different *meso*-substituents - see Milgrom et al, Tetrahedron, 1989, 45, 7431 and Milgrom, J. Chem. Soc., Perkin Trans. 1., 1984, 1483); also the presence
- 20 of separated peaks at higher field than TMS, i.e. two different protons inside the macrocycle suggest these porphyrin-like by-products may be isomers of 2b and 2c - containing 2-aza-21-carbaporphyrin macrocycle as described by Chmielewski et al, Chem. Eur. J., 1995, 1, 68.

Table 2 : UV/Visible Absorption Spectra of porphyrins in DCM

Porphyrin ^{a,b,c}	$\lambda_{\text{max}}/\text{nm}(\epsilon)^d$					
H ₂ TPP	417(417)	515(16.6)	552(8.9)	594(5.0)	650(4.0)	
H ₄ TPP ²⁺	439(411)		556(4.1)	604(11.0)	655(53.2)	
H ₂ I	451(371)		567(20.9)	606(57.5)	646(12.0)	710(14.1)
H ₂ 2a	463			621		717
H ₄ 2a ²⁺	485					726
H ₂ 2b	466(351)			599(sh)	642(67.2)	675(sh) 737(28.8)
H ₄ 2b ²⁺	488(311)					762(94.9)
H ₂ 2c	472(297)			600(sh)	653(89.1)	744(55.9)
H ₄ 2c ²⁺	496(189)					712(sh) 795(90.7)

^asee Falk, "Porphyrins and metalloporphyrins", Elsevier, Amsterdam 1975 for H₂TPP

^bsee Dalton et al, J. Chem. Soc. Perkin Trans 2., 1980, 370 for H₄TPP²⁺

^csee Anderson *ibid.* for H₂I

5 ^dDecadic extinction coefficient.

Other compounds of general Formula I may be prepared by corresponding methods to those described above. For example, trans-disubstituted *meso*-tetraethynylporphyrins in accordance with the present invention may be prepared by coupling acetylenic
 10 dipyrromethanes with substituted propynals. In general the synthesis involves reaction of arylethynyl dipyrromethanes with a variety of propynals. Thus arylethynyl dipyrromethanes were prepared in high yield via Lindsey's procedure. Chlorophyrins were synthesised by condensation of propynals prepared using literature methods with arylethynyl dipyrromethanes at -25°C in the presence of BF₃.OEt₂ as catalyst. DDQ
 15 oxidation of the resulting porphyrinogens gave high yields of chlorophyrins. Interestingly, no by-products of this synthesis were observed.

A preferred variation on this process involves protection of the acetylene moiety in the acetylene-aldehyde precursor with dicobaltoctacarbonyl. Following the
 20 preparation of the porphyrin, either by one-pot Lindsey synthesis or via the dipyrromethane, the protecting group is photochemically removed to afford the *meso*tetraarylethynylporphyrin in much improved yield.

Further examples of compounds in accordance with the present invention where A is phenyl are given below in Tables I and II; although A could just as easily be for example pyridine, pyrrole, pyrazine, imidazole, furan or thiophene.

TABLE I

Compound No.	R ₁	R ₂	R ₃	R ₄	Z	X	Y	X ₁	Y ₂	M
1.	-SiMe ₃	II	-SiMe ₃	II	-OC ₁₀ H ₂₁	H	H	H	H	2H
2.	-SiMe ₃	II	-SiMe ₃	II	-OC ₁₀ H ₂₁	H	H	H	H	Zn
3.	-SiMe ₃	II	-SiMe ₃	II	-OC ₁₀ H ₂₁	H	H	H	H	Ni
4.	-C ₆ H ₅	II	-C ₆ H ₅	II	-OC ₆ H ₁₃	H	H	H	H	2H
5.	-C ₆ H ₅	II	-C ₆ H ₅	II	-OC ₆ H ₁₃	H	H	H	H	Zn
6.	-C ₆ H ₅	II	-C ₆ H ₅	II	-OC ₆ H ₁₃	H	H	H	H	Pb
7.	-C ₆ H ₄ OC ₉ H ₁₉	II	-C ₆ H ₄ OC ₉ H ₁₉	II	H	H	H	H	H	2H
8.	-C ₆ H ₄ OC ₉ H ₁₉	II	-C ₆ H ₄ OC ₉ H ₁₉	II	H	H	H	H	H	Zn
9.	-C ₆ H ₄ OC ₉ H ₁₉	II	-C ₆ H ₄ OC ₉ H ₁₉	II	H	H	H	H	H	Cu
10.	II	II	II	II	H	-OC ₁₀ H ₂₁	-OC ₁₀ H ₂₁	H	H	2H
11.	II	II	II	II	H	-OC ₁₀ H ₂₁	-OC ₁₀ H ₂₁	H	H	Zn
12.	II	II	II	II	-OC ₁₀ H ₂₁	-OC ₁₀ H ₂₁	H	H	H	2H
13.	II	II	II	II	-OC ₁₀ H ₂₁	-OC ₁₀ H ₂₁	H	H	H	Zn
14.	II	II	II	II	-CN	-C ₁₀ H ₂₁	H	H	H	2H
15.	II	II	II	II	-CN	-C ₁₀ H ₂₁	H	H	H	Zn
16.	II	II	II	II	-F	H	H	H	H	2H
17.	II	II	II	II	-F	H	H	H	H	Zn

Compound No.	R ₁	R ₂	R ₃	R ₄	Z	X	Y	X ₁	Y ₁	M
18.	II	II	II	II	-CH ₂ F	H	H	H	H	2H
19.	II	II	II	II	-CH ₂ F	H	H	H	H	Zn
20.	II	II	II	II	-C ₄ H ₈ F	-C ₄ H ₈ F	H	H	H	2H
21.	II	II	II	II	-C ₄ H ₈ F	-C ₄ H ₈ F	H	H	H	Zn
22.	II	II	II	II	-NO ₂	H	H	H	H	2H
23.	II	II	II	II	-NO	H	H	H	H	2H
24.	II	II	II	II	-NO ₂	H	H	H	H	Zn
25.	II	II	II	II	-NO	H	H	H	H	Zn
26.	II	II	II	II	H	-N(C ₉ H ₁₉) ₂	H	H	H	2H ₃
27.	II	II	II	II	H	H	-N(C ₉ H ₁₉) ₂	H	H	Zn
28.	II	II	II	H	H	H	H	Cl	H	2H
29.	II	II	II	H	H	H	H	Cl	H	Zn
30.	II	II	II	H	H	H	H	H	-C ₁₀ H ₂₁	2H
31.	II	II	II	H	H	H	H	H	-C ₁₀ H ₂₁	Zn
32.	II	II	II	II	H	H	H	-OC ₉ H ₁₉	-OC ₉ H ₁₉	2H
33.	II	II	II	II	H	H	H	-OC ₉ H ₁₉	-OC ₉ H ₁₉	Zn
34.	II	II	II	II	H	H	H	-C ₉ H ₁₈ F	-C ₉ H ₁₈ F	2H
35.	II	II	II	II	H	H	H	-C ₉ H ₁₈ F	-C ₉ H ₁₈ F	Zn
36.	-F	II	H	II	-C ₁₀ H ₂₁	H	H	H	H	2H

Compound No.	R_1	R_2	R_3	R_4	Z	X	Y	X_1	Y_1	\bar{M}
37.	-F	II	H	II	-C ₁₀ H ₂₁	H	H	H	H	Zn
38.	-CHO	II	-CHO	II	-OC ₉ H ₁₉	F	F	H	H	2H
39.	-CHO	II	-CHO	II	-OC ₉ H ₁₉	F	F	H	H	Zn
40.	-OH	II	-OH	II	-C ₁₀ H ₂₁	H	H	H	H	2H
41.	-OH	II	-OH	II	-C ₁₀ H ₂₁	H	H	H	H	Zn ²⁴
42.	-OH	II	-OH	II	-C ₁₀ H ₂₁	H	H	H	H	Co
43.	-OH	II	-OH	II	-C ₁₀ H ₂₁	H	H	H	H	Mg
44.	-OH	II	-OH	II	-C ₁₀ H ₂₁	H	H	H	H	Mn
45.	II	II	II	II	-C ₁₀ H ₂₁	H	H	H	H	2H
46.	II	II	II	II	- (OCH ₂ CH ₂) ₃ - - (OCH ₂ CH ₂) ₃ -	- (OCH ₂ CH ₂) ₃ - - (OCH ₂ CH ₂) ₃ -	H	H	H	Zn

TABLE II

Compound No.	R ₁	R ₂	R ₃	R ₄	Z	X	Y	X ₁	Y ₁	I	Q	B	M
47.	II	II	II	II	H	III	H	H	H	-	-C ₉ H ₁₉	-C ₆ H ₄	2H
48.	II	II	II	II	H	III	H	H	H	-	-C ₉ H ₁₉	-C ₆ H ₄	Zn
49.	II	II	II	II	H	III	H	H	H	-CH ₂ O-	-F	-C ₆ H ₄	2H
50.	II	II	II	II	H	III	H	H	H	-CH ₂ O-	-F	-C ₆ H ₄	Zn
51.	II	II	II	II	H	III	H	H	H	-CH ₂ O-	-F	-C ₆ H ₄	Pd
52.	II	H	II	H	H	H	III	H	H	-COO-	-CN	-C ₆ H ₃ CH ₃)	2H
53.	II	H	II	H	H	H	III	H	H	-COO-	-CN	-C ₆ H ₃ CH ₃)	Zn
54.	II	H	II	H	H	H	III	H	H	-COO-	-CN	-C ₆ H ₃ CH ₃)	Al
55.	II	H	II	H	H	III	III	H	H	-NHCO-	H	C ₆ H ₄	2H
56.	II	H	II	H	H	III	III	H	H	-NHCO-	H	C ₆ H ₄	Zn
57.	II	H	II	H	H	III	III	H	H	-NHCO-	H	C ₆ H ₄	Ca
58.	II	H	II	H	H	III	III	H	H	-CONH-	-OC ₉ H ₁₉	-C ₆ H ₄	2H
59.	II	H	II	H	H	III	III	H	H	-CONH-	-OC ₉ H ₁₉	-C ₆ H ₄	Mg
60.	II	II	II	II	III	H	H	H	H	-OCH ₂ -	-N(CH ₃) ₂	-C ₆ H ₄	2H
61.	II	II	II	II	III	H	H	H	H	-OCH ₂ -	-N(CH ₃) ₂	-C ₆ H ₄	Mg
62.	H	II	H	II	H	III	III	H	H	-OOC	-NO ₂	-C ₆ H ₃ OCH ₃	2H
63.	H	II	H	II	H	III	III	H	H	-OOC	-NO ₂	-C ₆ H ₃ OCH ₃	Mg
64.	II	H	II	H	H	III	H	H	H	≡	-NO	-C ₆ H ₄	2H

<u>Compound No.</u>	R_1	R_2	R_3	R_4	Z	X	Y	X_1	Y_2	J	Q	B	M
65.	II	H	II	H	H	III	H	H	H	≡	-NO	-C ₆ H ₄	Mg
66.	II	H	II	H	H	III	H	H	H	≡	-NO	-C ₆ H ₄	Nb
67.	II	H	II	H	H	III	H	H	H	≡	-NO	-C ₆ H ₄	In
68.	II	H	II	H	H	III	H	H	H	≡	-NO	-C ₆ H ₄	Sn

An example of the use of a material and device embodying the present invention will now be described with reference to Figure 6.

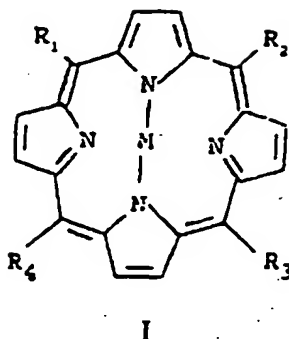
5 The Liquid crystal device consists of two transparent plates, 1 and 2, for example made from glass. These plates are coated on their internal face with transparent conducting electrodes 3 and 4. An alignment layer is introduced onto the internal faces of the cell so that a planar orientation of the molecules making up the liquid crystalline material will be approximately parallel to the glass plates 1 and 2. This is done by coating the glass plates 1,2 complete with conducting electrodes 3,4 with
10 layers of film 5 and 6 of a suitable polymer, e.g. polyimide. The electrodes 3,4 may be formed into row and column electrodes so that the intersections between each column and row form an x,y matrix of addressable elements or pixels. Prior to the construction of the cell the films 5,6 are rubbed with a roller covered in cloth (for example made from velvet) in a given direction, the rubbing directions being arranged
15 parallel (same or opposite direction) upon construction of the cell. A spacer 7, e.g. of polymethyl methacrylate, separates the glass plates 1,2 to a suitable distance, e.g. 2 microns. Liquid crystal material 8 is introduced between glass plates 1,2 by filling the space in between them. This may be done by flow filling the cell using the standard techniques. The spacer 7 is sealed with an adhesive 9 in a vacuum using an existing
20 technique. Polarisers 10,11 may be arranged in front of and behind the cell.

Alignment layers may be introduced onto one or more cell walls by one or more of the standard surface treatment techniques such as rubbing, oblique evaporation or as described above by the use of polymer aligning layers.
25

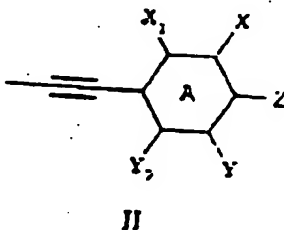
The device may operate in a transmissive or reflective mode. In the former, light passing through the device, e.g. from a tungsten bulb, is selectively transmitted or blocked to form the desired display. In the reflective mode a mirror, or diffuse reflector 12 is placed behind the second polariser 11 to reflect ambient light back
30 through the cell and two polarisers. By making the mirror partly reflecting the device may be operated both in a transmissive and reflective mode. In an alternative embodiment a single polariser and dye material may be combined.

CLAIMS

1. A compound of general Formula I:



wherein R_1 , R_2 , R_3 and R_4 are each independently H, optionally substituted alkyl, optionally substituted alkoxy, optionally substituted alkenyl, optionally substituted alkenyloxy, $\text{Si}(\text{alkyl})_3$, halogen, CHO, COOR_5 , OH, CN, NO_2 , NO, NR_5R_6 or the following Formula II:



wherein



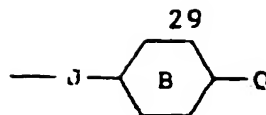
is optionally substituted aryl or optionally substituted heteroaryl;

R_5 and R_6 are each independently hydrogen, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted aryl, halogen or hydroxy;

X, Y, X_1 , Y_2 and Z are each independently H, optionally substituted alkyl, optionally substituted alkoxy, optionally substituted alkenyl, optionally substituted alkenyloxy,

$\text{Si}(\text{alkyl})_3$, halogen, CHO, COOR_5 , OH, CN, NO_2 , NO, NR_5R_6 , any adjacent two

groups taken together form a $-(\text{OCH}_2\text{CH}_2)_n-$ group wherein n is 1, 2 or 3, or the following Formula III:



III

5 wherein J is a single bond, \equiv , CH_2O , OCH_2 , COO , OOC , NHCO , CONH , CH_2 or O ;

Q is H, optionally substituted alkyl, optionally substituted alkoxy, optionally substituted alkenyl, optionally substituted alkenyloxy, $\text{Si}(\text{alkyl})_3$, halogen, CHO , COOR_5 , OH , CN , NO_2 , NO , NR_5R_6 ;

10



is optionally substituted aryl or optionally substituted heteroaryl;
provided that at least one of R_1 , R_2 , R_3 or R_4 is selected from Formula II;

15 M is 2H with each of the two nitrogen atoms indicated being bonded to a single hydrogen, or M is a metal atom, metal compound or silicon or a compound of silicon.

2. A compound according to claim 1 wherein R_1 , R_2 , R_3 and R_4 are each independently H, C_{1-20} alkyl, halogen, CHO , OH or the group of Formula II, wherein

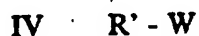
20 A is phenyl; Z is selected from H, C_{1-20} alkyl or alkoxy, CN , NO_2 , NO , $\text{N}(\text{C}_{1-20} \text{alkyl})_2$; X_1 and Y_2 are independently selected from H, halogen, C_{1-20} alkyl or alkoxy, C_{1-20} haloalkane;

X and Y are each independently chosen from H, halogen, C_{1-20} alkyl or alkoxy or a group of Formula III, wherein J is as defined in claim 1, Q is H, C_{1-20} alkyl or
25 alkoxy, CN halogen, NO_2 , NO , $\text{N}(\text{C}_{1-20} \text{alkyl})_2$; B is phenyl and, in addition to H, may be substituted with at least one of the following groups: halogen, C_{1-20} alkyl or alkoxy.

3. A compound according to claim 1 or claim 2 wherein the metal atom is Ni,

30 Pb, V, Pd, Co, Nb, Al, Sn, Zn, Cu, Mg, Ca, In, Ga, Fe, Eu, Lu, Pt, Ru, Mn or Ge.

15. An optical storage medium comprising a compound of any one of claims 1 to 9 or a composition of claim 10.
- 5 16. A optical recording medium comprising a compound of any one of claims 1 to 9 or a composition of claim 10.
- 10 17. A device comprising two spaced cell walls each bearing electrode structures and treated on at least one facing surface with an alignment layer, a layer of a liquid crystal material enclosed between the cell walls, characterised in that the liquid crystal material comprises a compound of any one of claims 1 to 9 or a composition of claim 10.
- 15 18. A process for preparing the compound of any one of claims 1 to 9 comprising reacting at least one intermediate of Formula IV



where R' is at least one of R₁, R₂, R₃ or R₄ with pyrrole.

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Fig.1.

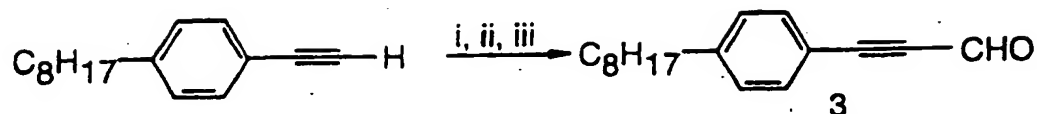


Fig.2.

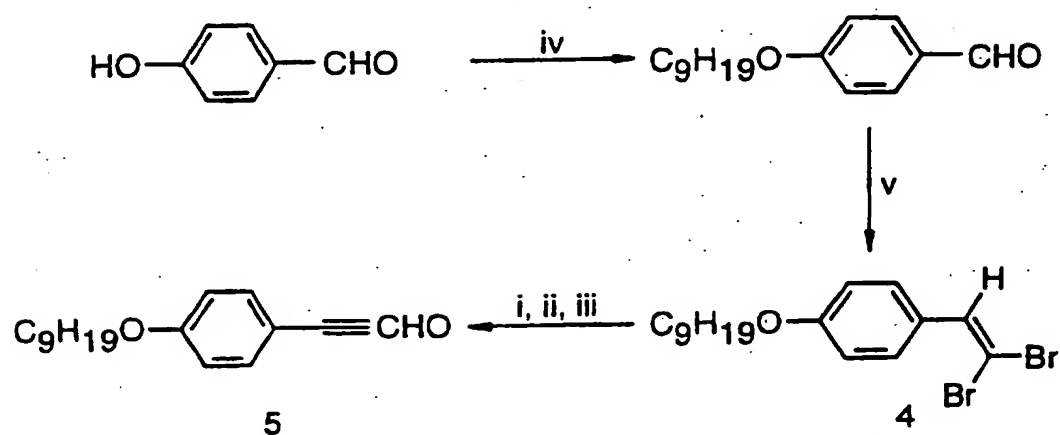
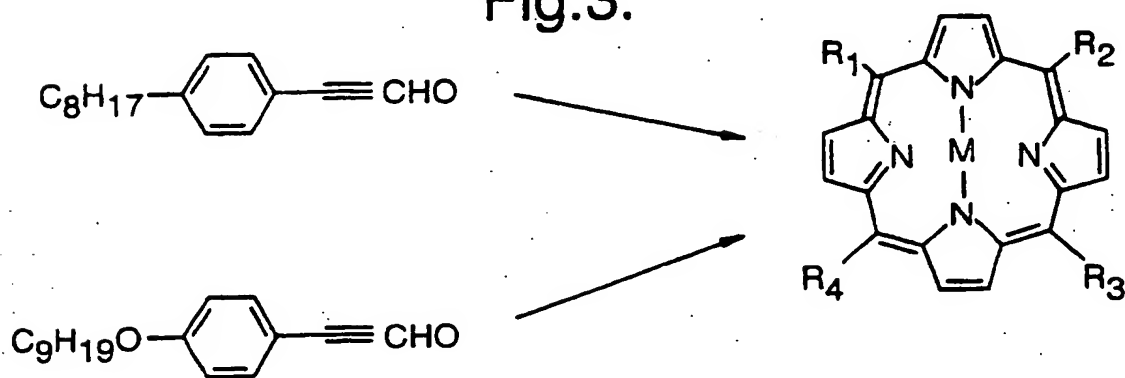
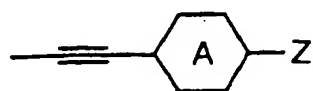


Fig.3.

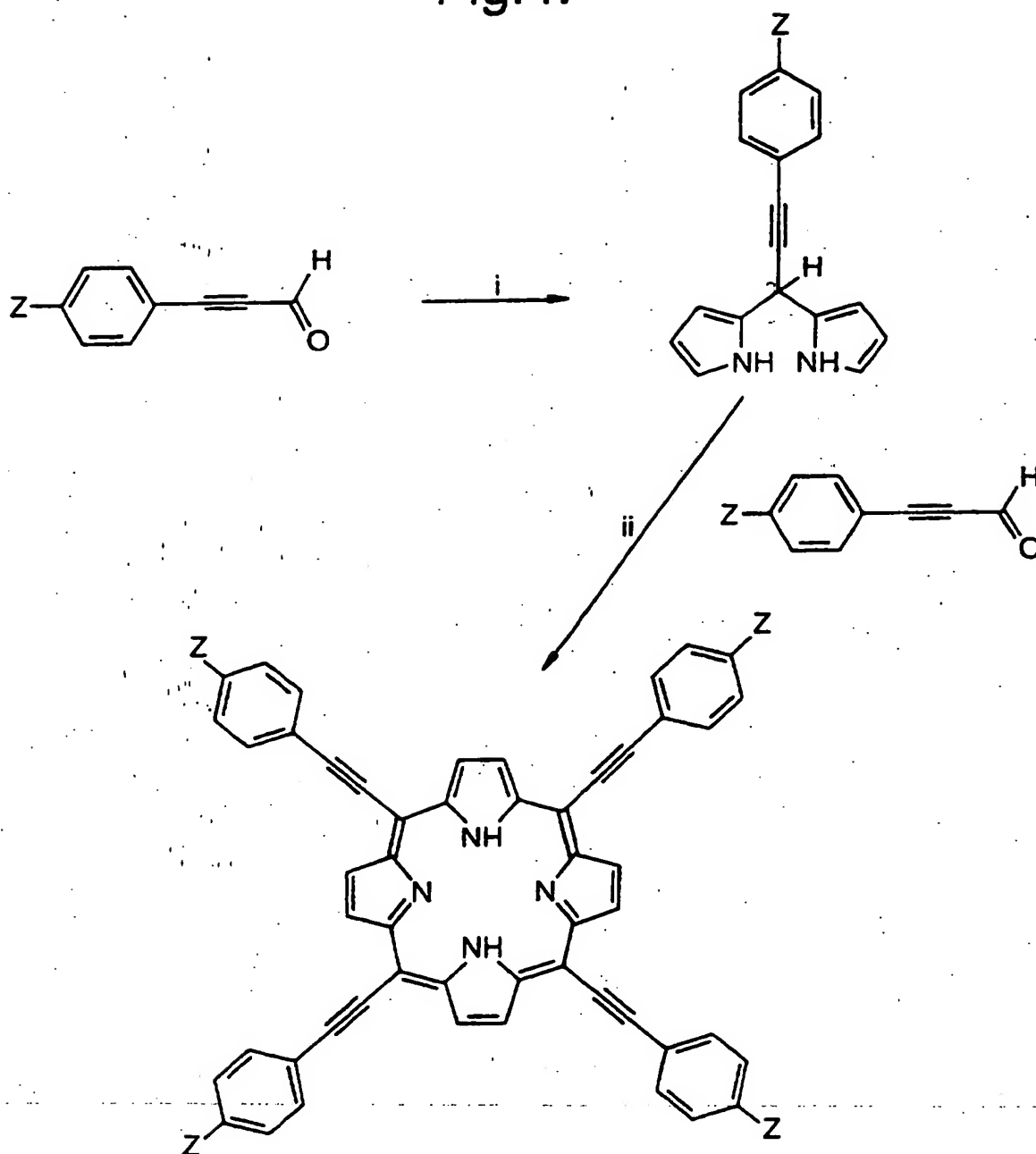
R₁-R₄ ARE ALL:

2a: Z=H

2b: Z=C₈H₁₇2c: Z=OC₉H₁₉

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Fig.4.



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Fig.5.

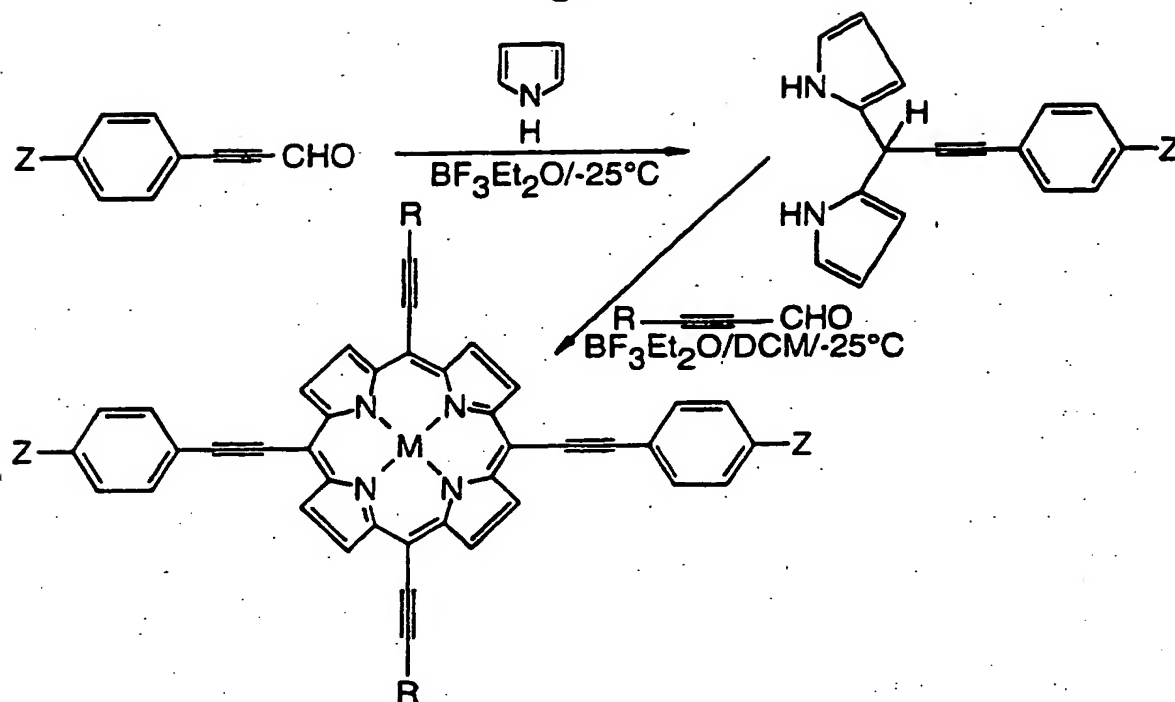
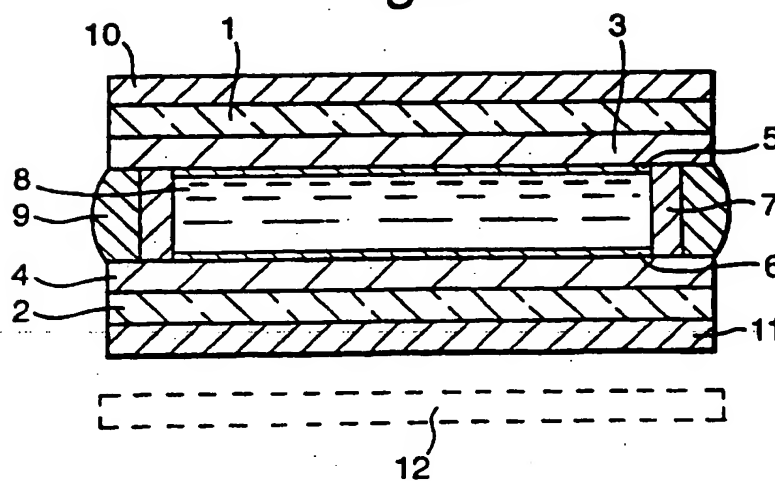


Fig.6.



INTERNATIONAL SEARCH REPORT

national Application No
PCT/GB 96/02899

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07D487/22 A61K31/40 C09K19/34 //(C07D487/22,257:00,
209:00,209:00,209:00,209:00)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	TETRAHEDRON LETTERS, vol. 33, no. 2, 1992, OXFORD GB, pages 269-272, XP002030190 G. PROESS ET AL.: "Synthesis of meso-tetraalkyl porphyrins using 1-seleno-2-alkynyl cation precursors" see compound 5b	1
A	US 5 252 698 A (BHARDWAJ ET AL.) 12 October 1993 see column 8, line 25 - line 31; claim 1	9,11
P,X	TETRAHEDRON LETTERS, vol. 36, no. 49, 1995, OXFORD GB, pages 9061-9064, XP002030191 L.R. MILGROM ET AL.: "5,10,15,20-meso- Tetraarylethynylporphyrins" see whole article	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

24 April 1997

Date of mailing of the international search report

23 -05- 1997

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 96/02899

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	<p>TETRAHEDRON LETTERS, vol. 37, no. 23, 1996, OXFORD GB, pages 4069-4072, XP002030192 L.R. MILGROM ET AL.: "Trans-disubstituted meso-tetraethynylporphyrins" see whole article</p> <p style="text-align: center;">-----</p>	1

